The Atomic Weight of Copper by Electrolysis

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I. INTRODUCTION.

The following is an account of the determination of the relative weights of copper and silver deposited when the same electric current passes through copper and silver voltameters. For the successful determination of the relative weights by the electrical method several important effects have to be borne in mind :—

1. *The solution of the deposited metal* in the liquid of the cell. In a preliminary investigation it was found that if the solution

was assumed to be proportional to the area of the cathode very concordant results were obtained for the corrected values of the ratio of the deposited weights of copper to that of silver. In this way the mean error in the value of the ratio for nine early experiments was altered from 1 part in 500 to 1 part in 6,000. In order to apply the solution correction four copper cells in series, having different cathode areas, were used in the final experiments. By a graphical construction the amount which would have been weighed on a cathode, free from loss by solution, was always taken as the corrected weight of the copper deposited in the cell. In the case of silver this correction was found to be unnecessary, and therefore in the final work the silver was determined by taking the mean of the weights of the deposits of two silver cells, these cells being separated by four others in which copper was deposited.

2. The cathode current density must be kept *below a certain limiting value*, depending upon the concentration of the electrolyte, the amount of acid present and the geometry of the cell. If this value is exceeded the deposit is non-coherent, powdery in consistency and apparently amorphous. Experiment shows that such deposits do not yield concordant results on weighing. In order to determine the limiting current-density a series of experiments in which the conditions were varied systematically was carried out. The chief result obtained was that in all cases the deposition of unweighable metal was heralded by a rise in the reading of a voltmeter placed across the cell. Under the heading of "Limiting Current Density" (Section II.) the method of predetermining the safe current for any cell is explained. In the final determinations the information thus gained is utilised so as to permit the employment of widely varying current densities, all, however, well under the limiting values.

3. A deposit may, however, be unsatisfactory in other ways. Visible crystalline growths, liable to be lost in washing or weighing, may present themselves. Coarse-grained deposits of this type may also do harm by imprisoning some of the electrolyte. The allowable current density in this case depends upon the weight to be deposited—the greater the amount to be deposited the lower must be the current density. By rotating the cathodes, or by using porous pots, both the weight deposited and the current density may be increased. These points are further considered under the heading "Crystalline Growths" (Section III.).

4. Before the final determinations were made the effects of impurities in the cell were investigated. These effects were either nil or were eliminated by using suitable current densities, by rotating the cathodes, or by using porous pots. Details are discussed under the heading "Impurities" (Section IV.).

5. It was found to be essential that the changes in the weights of the deposits, due to exposure in drying and weighing, should be eliminated by equal treatment of all the deposits in each experiment. The graphical method of correcting for loss by solution will then at the same time correct for oxidation, &c., if the washing and drying be done simultaneously for all the deposits.

II. THE LIMITING CATHODE CURRENT DENSITY.

1. *The Cylindrical Cell.*

The deposits obtained in the common types of cells are far from being uniform, especially with parallel plate electrodes, where the deposit on the edges is often granular and non-coherent. The cylindrical cell was finally adopted because it gives uniform deposits and allows, other things being equal, a higher current density to be used. A cell of this type, a copper voltameter, is shown in the accompanying diagram (Fig. 1). The anode consists of a copper tube. For other metals the anode foil is kept in position by xylonite tubes, which drop into circular slots cut in the base, and are fixed with paraffin wax. The cathode consists of a brass rod. The brass cap, shown in position, need only be used when it is desired to rotate the cathode, the cap and the V-shaped slot then being amalgamated. Sometimes it is necessary to introduce porous partitions between the electrodes. These are the ordinary battery porous pots, the top being cut off to the required length. After being cleansed by boiling successively with aqua regia, potassium cyanide, nitric acid and water, they, too, are dropped into circular grooves and fixed in position with paraffin wax. It is important that there should be no leakage under the pot.

2. *Deposition of Hydrogen.*

Suppose we take the copper cell just described, fix the cathode and add a solution of copper sulphate. Let the current be gradually increased and the deposit examined from time to time. At first the deposit is bright, metallic, coherent and uniform throughout. After a time the deposit immediately below the surface of the electrolyte becomes tarnished

and then quickly develops into a chocolate coloured non-coherent mass. As time proceeds, or the current is raised further still, this non-coherent mass extends from the upper

FIG. 1.—THE CYLINDRICAL VOLTAMETER.

part of the electrode downwards, quickly at first and then gradually more slowly. If the current is sufficiently high this

will be succeeded by the evolution of hydrogen. A voltmeter placed across the cell indicates an increase in voltage simultaneously with the deposition of the chocolate mass. This change in the character of the deposit is not due to the anode, since covering it with two or three layers of filter paper makes no difference. Neither is it due to the atmosphere, because in one experiment two identical cells were run in series, one having the electrolyte covered with a layer of oil. In both the effect appeared at the same time and to the same extent. Nor does the amorphous mass consist of copper oxide, since a portion of it, after being cleaned, dried and weighed, was reduced in a stream of hydrogen, and when re-weighed showed no loss in weight. The appearance of this deposit is similar to that of copper precipitated from a solution of copper sulphate by means of zinc. The same phenomenon is observed in other cells, the non-coherent deposit for zinc being bluish grey, for silver a dirty grey and for gold an orange red. In all cases, however, provided that the cathode current density is below a definite value, the action never takes place. On the other hand, if the current density (d) be raised above a certain value, the whole of the current cannot be carried by the copper ions, and some of it must be carried by the hydrogen ions. When the latter are deposited they interfere with the deposition of the copper, and hence give rise to the non-coherent deposit. When the rate of deposition becomes greater hydrogen will be evolved as gas. The copper thus deposited becomes so voluminous that it greatly increases the effective area of the cathode, consequently the cathode current density is reduced below the critical value for the deposition of hydrogen, and the copper is deposited in the metallic state again, the deposit then having the appearance of a gnarled oak stem. Hence, in order that the deposits may yield concordant results, it is necessary that the cathode density should be below a certain maximum or limiting value.

3. *The Methods of Obtaining the Limiting Current Density, "D."*

There are two ways of obtaining the value of D , the maximum or limiting cathode current density, namely, the weighing and voltmeter methods.

(a) *The Weighing Method.*—In a given cell systematically increased currents are run for the same length of time. The weights of the deposits are proportional to the currents. When, however, the copper is deposited by the secondary reaction

the deposit when weighed will no longer be proportional to the current. By a graphical construction this point of departure is found, and gives the maximum current which can be used. From this the limiting current density is deduced. This method is chiefly applicable to the case of rotating cathodes.

FIG. 2.—THE RISE IN VOLTAGE WHEN THE LIMITING CURRENT IS EXCEEDED.

(b) *The Voltmeter Method.*—A more expeditious method was found by placing a voltmeter across the cell, and noting its readings for steady increments of current. This gives the ordinary ohmic straight line passing through the origin, the line OAB of Fig. 2, which is the graph for one experiment.

But if the current is 0.8 ampere the needle, after standing at B for a time, begins to rise slowly at first, and then with increasing speed till the point C is reached, where it remains stationary or gradually falls. An examination of the cathode shows the presence of the non-coherent deposit. If the current is high enough the needle oscillates about the maximum reading, the amplitude of the oscillation giving a rough measure of the rate of the evolution of hydrogen. The curve passing through the maximum readings cuts the line OAB at A.

FIG. 3.—TIME FOR THE VOLTAGE TO RISE TO THE HIGHER VALUE WHEN THE LIMITING CURRENT IS EXCEEDED.

Below this point there is no trace of the non-coherent deposit. The point of intersection is taken as the limit to which the cell can be safely run. From this the value of D is deduced. In this experiment the cathode was cleaned before each reading. If this is omitted then the graph consists of the broken line OAC. Fig. 3 is for the same experiment, but in this case the ordinates represent the time in seconds for the voltage to rise to its higher value, after the switching on of the current. This curve can be represented by the equation $T = a(C - C_0)^{-b}$,

where C_0 is the distance of the vertical asymptote from axis of time, *i.e.*, with a current equal to, or below, C_0 the time for secondary deposition to take place is infinite. In this case the value for C_0 , the limiting current, is equal to 0.35 ampere, the same as for the point A in Fig. 2.

The voltmeter method is capable of further modification to meet particular cases. By these methods the value of D was found for the voltmeters of copper, silver, gold, and zinc under varying conditions of:—concentration of the electrolyte, height and radial thickness of the cell, change of temperature, the addition of acid and other impurities to the electrolyte, the inclusion of a porous pot, and the rotation of the cathodes.

4. *The Value of the Limiting Current Density, "D."*

The following empirical formula was found to give the limiting cathode current density for the electrolytes copper sulphate, zinc sulphate, silver nitrate, and gold chloride, the last containing acid,

$$D = ab^x c^y d^z, \quad \dots \quad (1)$$

where D is measured in amperes per square centimetre. The values for the quantities are given in the table below.

Cell.	a.	c.	d.	x.	b.	y.	z.
Cu	0.0525	0.94	1.06	1.11	Concentration of the electrolyte in terms of normal strength.	Height of the cathode in cs. between the limits 3-7 cs.	Radial thickness of the electrolyte in cs. between the limits 2-4 cs.
Zn	0.0534	0.94	1.06	1.09			
Ag	0.094	0.94	1.06	1.33			
Au	0.050	0.94	1.06	1.14			

In this table b , c , d , y and z are independent of the particular metal, whilst a and x are peculiar to each metal. Further, it was found that in the case of Cu, Zn and Ag the limiting current density can be expressed by the formula

$$D = e(1-\alpha)wc^y d^z, \quad \dots \quad (2)$$

in which ab^x in equation (1) is replaced by $e(1-\alpha)w$. Here $e(=2.13)$ is a constant, the same for the three metals, $(1-\alpha)$ is the un-ionised fraction of the salt in solution, and w is the mass of the metal per cubic centimetre. The equation (2), written in full, becomes

$$D = 2.13 (1-\alpha)w(0.94)^y(1.06)^{x_1-x_2}. \quad \dots \quad (2A)$$

In 45 cases the calculated and experimental value of D agreed within the limits of experimental error. From equation (2A) it is evident that the value of D depends upon the geometry

of the cell, and also to a large extent upon the density convection currents.

Temperature.—All the above equations apply more particularly to the case in which the temperature of the laboratory and the electrolyte is about 18°C. If, however, the temperature rises, the new value of the constant (e) in equation (2) is given by

$$e_t = e_{18} + 0.05(t - 18^\circ). \quad . \quad . \quad . \quad . \quad (3)$$

Porous Pots.—If the electrodes are separated by porous pots the convection currents due to the removal of the metal ion are greatly restricted, and the allowable D falls in consequence. The new value for D is still given by the equations (1) and (2), but (z) is now reduced to zero.

Acids.—The allowable current-density is also cut down by the presence of acid in the cases of Cu, Zn and Ag, and if D be calculated from equations (1) and (2), which is for neutral solutions, the actual allowable current-density is found to be given by the equation

$$D_a = D(0.93)^n, \quad . \quad . \quad . \quad . \quad (4)$$

where n is the concentration of the acid in terms of $N/10$ strength.

Rotation of the Cathodes.—The value of D rose when the cathode was rotated in the case of Cu and Zn, whether a porous pot was used or not, according to the equation

$$D_R = D(1 + 0.0024R), \quad . \quad . \quad . \quad . \quad (5)$$

where R is the number of revolutions per minute. The results for silver in this case were not conclusive.

It thus appears that, provided cylindrical cells are used, the maximum safe current can be calculated for all conditions imposed upon the experiment.

III. CRYSTALLINE GROWTHS.

Having arranged that the value of the cathode current-density (d) shall be sufficiently small to satisfy the previous rules, it is still necessary to restrict the total amount of deposit in order to avoid difficulties from crystalline growths. This is given by the simple empirical equation

$$w\Delta = \text{constant}, \quad . \quad . \quad . \quad . \quad (6)$$

where w is the total number of grammes deposited on a cathode

and Δ is the maximum current-density at which these crystal-line growths are not produced. The value of the constant for different conditions of the cell is given in the accompanying table.

Metal.	Electrolyte.	Porous pot.	Rotation of cathode.	$w\Delta$.
Copper	Neutral	None	Stationary	0.025
	Neutral	Porous pot	Stationary	0.05
	+ $\frac{1}{15}\%$ of H_2SO_4 by volume	Porous pot	Stationary	0.025
	Idem	Porous pot	1,000 r.p.m.	0.035
Silver	Neutral	None	Stationary	0.08
	Neutral	None	600 r.p.m.	0.08
	Neutral	Porous pot	700 r.p.m.	0.2

It is necessary, therefore, to use in any experiment a (d) less than either D or the Δ calculated from the above table.

IV. IMPURITIES IN THE CELL.

1. *Anode Detritus.*

Very soon after the current is started a density convection current of the electrolyte is set up. This current, descending at the anode and ascending at the cathode, carries with it anode detritus. This gives rise to coarse coralline deposits at the bottom of the cathode. Covering the anode with a few layers of filter paper makes no improvement. Rotating the cathode diminishes this effect to an extent depending on the rate of revolution, but a trace of it is sometimes seen in the form of a spiral on the rod, which may in silver develop into fan-like plates. The trouble is eliminated by separating the electrodes with a porous pot. In this case copper oxide, sand and pumice powder may be held in suspension in the electrolyte without materially affecting the deposit. It seems, therefore, that only very small particles, which can pass through filter paper but not through a porous pot, can act as nuclei for the formation of the coralline bottom growths.

2. *Acid.*

Acid added to the cell clarifies the electrolyte and decreases the anode detritus. Besides lowering the value of D it modifies the character of the deposit considerably. The normal deposits of copper and silver consist of octahedral crystals. In the case of copper, if the current-density is above 0.01, the

crystalline deposit is destroyed. In its place we have a creamy non-crystalline surface, and on this hemispherical protuberances appear, increasing in number and size with time, till they become contiguous, and then develop into a coralline structure. Deposits from acidified solutions give concordant weighings, provided that the experiment is kept within the $w\Delta$ limits of equation (6). On the other hand, the crystalline deposit of silver is not destroyed, but in the upper region of the cathode needle-shaped crystals soon appear, which, branching, develop into beautiful lace-like patterns. For this reason, in the final determinations, only neutral solutions of silver nitrate were used.

3. *Other Added Impurities.*

The following impurities were introduced in the preliminary experiments to test the effect on the value deduced for the atomic weight. In the copper cell were introduced ZnSO_4 , FeSO_4 , AgNO_3 and CaCl_2 ; and in the silver cell $\text{Cu}(\text{NO}_3)_2$.

(a) The presence of AgNO_3 in the electrolyte was at once detected by the silver being precipitated from the solution on the electrodes. The CaCl_2 immediately blackens the cathode, and causes the needle of a voltmeter when placed across the cell to give very unsteady readings.

(b) The presence of ZnSO_4 , FeSO_4 or $\text{Cu}(\text{NO}_3)_2$ in the electrolyte lowers the value of D the same as acids do according to equation (4).

(c) Neither Zn nor Fe is deposited in the copper cell. In a particular experiment the electrolyte contained equal parts of Cu and Zn. Using a current-density of 0.013, a deposit having a beautiful matt surface was obtained. This was peeled off, and 0.323 gramme of it dissolved. The copper precipitated as $\text{Cu}(\text{CNS})_2$ yielded 0.322 gramme. Clearly, therefore, no zinc was deposited. Graham obtained a similar result with iron, the proportion of Cu to Fe in the electrolyte being 3 to 2.

Neither is Cu deposited from a silver cell. Repeating the experiment of Lord Rayleigh and Mrs. Sidgwick, but having a higher copper content, the proportion of Ag to $\frac{1}{2}\text{Cu}$ being 5 to 1, a good deposit was obtained. 0.9437 gramme of the deposit was dissolved, and the silver, precipitated as AgCl , gave 0.9436 gramme. These experiments cover practically all the impurities likely to be present in the two electrolytes.

4. *The Purity of the Metals and Salts used in the Final Determinations.*

In the final work no difference in the results was obtained when the electrodes consisted of the ordinary laboratory metal, or the extra pure of Kahlbaum, and the same is true for the salts copper sulphate, and silver nitrate.

V. AN ACCOUNT OF PREVIOUS WORK.

The solution of the Cu cathode by the electrolyte was first pointed out by Goré (1). Gray (2) also showed that this effect varied with the different conditions of the cell. Richards and Collins (4) found that the loss in weight of a cathode was proportional to its area. The loss was little affected by the presence of acid, but increased with the concentration of the electrolyte. This confirmed the work of Foerster and Seidel (19). They pointed out that the Cu dissolves in a strong CuSO_4 solution to form Cu_2SO_4 , which may, especially in neutral solutions, yield too high a result, due to the presence of cuprous ions. Schuster (20) also showed that the solvent power of acid in the electrolyte was small. Experiment, however, showed that the solution effect cannot be corrected for by control experiments, especially as Adams and McNutt (3) proved that it is only the freshly deposited Cu which is so sensitive to the action of acid. The graphical method of correcting for solution under experimental conditions showed that the solvent power of the electrolyte does not increase with its concentration, but does increase with the acid content. The effect sometimes encountered with electrolytes previously boiled over Cu, where the weight of Cu deposited increases with the area of the cathode, may be looked upon as due to oxidation, which can be easily corrected for by the graphical method. If, however, Cu_2SO_4 is formed in the cathode space, its concentration and the amount of deposition by the cuprous ions will still be a function of the cathode area. Hence the graphical method of correction will cover this case, too. This method is preferable to that adopted by Beach (5) and Shephard (6), who added arbitrary amounts of ammonium chloride to their neutral electrolytes to prevent oxidation.

The amorphous deposit discussed in section II. was noted as far back as 1844 by Smee (7). Le Blanc (8) considered that both copper and hydrogen ions are present at the cathode, but the latter are not liberated until the concentration of the

copper ions is reduced to zero. Sand (9), using a vertical cell, came to the same conclusion. But Hittorf (10), as quoted by Sand, believed that the two ions are deposited at all current-densities. The hydrogen, however, reacts with copper sulphate with a definite reaction velocity, and is only evolved when its rate of deposition is greater than the reaction velocity. It seems from the experiments on the limiting current-density that more probably a definite cathode fall in potential is necessary for the deposition of hydrogen.

In order to increase the effective cathode current density Graham (11) circulated his electrolyte. Experiment shows, however, that better results are obtained when the cathode is rotated. The rotation of the cathode is employed by Cowper-Coles (12) for the deposition of copper on an industrial scale. He obtains a smooth deposit, which he maintains is due to the skin friction between the electrode and the electrolyte. Smooth deposits were not obtained in my experiments which may be due to the peripheral speed being insufficient. Also to eliminate the coral growths, due to anode detritus, he surrounds the bottom of the cathode with a baffle plate, placed a short distance away from it.

A résumé of the work on the silver voltameter is given by Guthe (13). This contains an account of the Guthe-Richards cell, which was used in the final determinations of the Atomic Weight in this Paper. The work of Lord Rayleigh and Mrs. Sidgwick (17), and that of Smith, Mather and Lowry (18), will be referred to in the next section.

The earlier determinations of the atomic weight of copper, chiefly performed by the reduction of CuO , were vitiated by systematic errors. This was pointed out by Richards (14). In his classic work he estimates the combining weights of Cu and Br in CuBr_2 ; the Cu, two determinations, by its deposition from 50 cc. of solution by electrolysis, and the bromine, six determinations, by precipitating it as AgBr . By combining these results 12 values for the atomic weight are obtained, whose mean is 63.57—the accepted value in the 1913 list of atomic weights, where $\text{O}=16$, $\text{Ag}=107.88$. Shaw (15), by the electrolytic deposition of Cu and Ag from cells in series, the Cu being deposited on 1 to 16 platinum wires, obtained the atomic weight 63.46. He endeavoured to correct for solution as a function of the current density. In the preliminary experiments of this Paper similar corrections gave abortive results. Using a silver cell of the Rayleigh and Sidgwick

type, and two copper cells of the parallel plate type, Richards and Collins (4) obtained the value 63.534, with a mean error of 0.02 for the last six consecutive determinations. This value is for the corrected weight of Cu found by extrapolating to zero area, the same as explained in this Paper. Unfortunately only two plates were used, and no note is given to say if they were simultaneously washed and dried. Subsequent work by Richards and Heinrod (21) showed that the weight of Ag deposited in the cell of the Rayleigh and Sidgwick type was greater than that obtained when a porous pot surrounds the anode. The correction for this raised the atomic weight of copper to 63.560. Also they found that by heating the Ag deposit to redness the deposit lost in weight. This further correction raised the atomic weight to 63.571. Lastly Pécheux from a similar electrolysis with neutral solutions, obtained the value 63.43. No details are given in the Paper referred to (16).

VI. THE ATOMIC WEIGHT OF COPPER.

In the following determinations two silver cells separated by four copper cells were run in series. This will correct for any short circuiting of the current. The ratio of the corrected weight of the deposits of copper to that of silver was found. From this the atomic weight of copper

$$= \frac{\text{Weight of copper}}{\text{Weight of silver}} \times 2 \times 107.88.$$

The solution of the copper deposit was corrected for by the graphical method. This necessitated simultaneous washing and drying of the electrodes. The maximum cathode current density used must be less than that calculated from the equations (1) to (5). Also for a given weight of metal to be deposited the greatest current density used must be less than that given in equation (6).

1. *The Silver Cells.*

The cylindrical cell with a silver rod for cathode allowed only a small range of current densities to be used. As larger cathodes were not at my disposal the Guthe-Richard's cell was used. This is a modification of that of Lord Rayleigh and Mrs. Sidgwick (17). The cathode consists of a platinum dish, which is separated from the anode by a porous pot, the anode plate being tightly packed in with fine grains of silver, chiefly obtained from previous deposits. The silver nitrate

was freed from acid by fusing the salt before dissolving it. Although the equations already considered do not numerically apply to this cell yet similar phenomena are observed. The safe limits for the deposited weight and the current density were obtained from the preliminary experiments. The deposit, after being thoroughly washed and dried, was weighed. Afterwards it was heated to redness, and, when cool, reweighed. From the difference in the two weighings the correction for the occluded salt was obtained, after Lord Rayleigh and Mrs. Sidgwick.

2. *The Copper Cells.*

These were all of the cylindrical type. The determinations recorded (1) to (4) were the last of the series in which rotating cathodes were used, numbers 1 and 2 being carried out prior to the investigation of the effects of the porous pot. Determinations 5 to 10 are the last six experiments carried out. These were performed after all the preliminary work was completed and form an unbroken set of results, none of the weighings being omitted, except that in brackets in number 5. This is explained in the footnote at the end of the table. All the cells contain porous pots except those of the first two, 3 and 4 have red pots and the rest white ones. In the experiments 1 to 4, as soon as the current was broken rotation was stopped, and the rods were dropped into a similar copper sulphate solution as quickly as possible. The caps were removed, the rods simultaneously rinsed in tap water, and distilled water, allowed to stand in absolute alcohol, wiped with a cloth desiccated, and weighed. It was found that the areas of the cathodes did not vary sufficiently to plot the graph satisfactorily. In the experiments 5 to 10 with stationary cathodes the following modifications were adopted. On a single teak base were arranged four pillars of the same height, carrying the slotted brass plates, which could be swung out of position easily. The whole was heavily coated with shellac varnish. The cells consisted of two battery jars and two crystallising dishes, the latter being raised on teak blocks. White porous pots were added and paraffin wax run in until the appropriate depth was obtained. When the cells were in position, the tops of the porous pots, which reached half a centimetre above the cells, were on the same level. Three of the four cathodes consisted of thin brass tubes, closed at each end with brass discs. They were 12 to 16 cs. long and 2 cs. in diameter. The fourth cathode was a brass rod. The remaining portions of the cells

TABLE I.—CONDITIONS OF EXPERIMENT.

No.	Strength of AgNO_3 solution.	Strength and state of CuSO_4 solution.	Rotation of cathodes. R.P.M.	Current in amps.	Time in mins.	Current density of Cu cathode.		Solution factor $\times 10^{-5}$.	Notes.
						Max.	Min.		
1	2.5—N {	2.5—N + 0.3% acid }	720	1.0	33	0.10	0.063	—2.0	1 rod stopped resulting in the current density being too high.
2	2.5—N {	2.5—N + 0.3% acid }	700	1.0	65	0.14	0.067	—6.7	Cu reduced in hydrogen.
3	2.5—N {	2.0—N neutral ; boiled over Cu on water bath for 2 hours. }	(a) 0 (b) 600 } 0.6	55	0.045	0.014	{ (a)+0.32 (b)+0.75 }	(a) 2 hollow tubes. (b) 3 rods.	
4	2.5—N {	1.8—N neutral(?); boiled 3 times as above. }	830	0.6	54	0.056	0.038	—6.1	
5	1.0—N {	2.0—N + 0.1% acid }	Stationary.	0.2	240 + 90	0.018	0.0037	—6.6	During absence the circuit was broken after 240 mins., so electrodes stood in electrolyte for another 90 mins.
6	1.0—N	Idem.		0.23	155	0.02	0.0042	{ $\frac{-1.6}{-2.2}$ } —1.9	Deposit on copper
7	2.0—N	Idem.		0.2	270	0.019	0.0038	{ $\frac{-4.6}{-4.2}$ } —4.4	
8	2.0—N {	2.0—N neutral ; water bath for 2 hours. }		0.23	275	0.021	0.0042	0	Anodes of Kahlbaum's Cu.
9	1.9—N filtered {	2.0—N, water bath for 2 hours, +0.1% acid. }		0.175	430	0.016	0.0033	—3.6	
10	1.9—N filtered {	Idem., used 2nd time. }		0.3	120	0.025	0.0055	—0.66	1 new porous pot for Ag, well boiled after chemical treatment

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followed the type previously described under the heading "Cylindrical Cell." The copper sulphate solution was poured into the cells to the same distance from the top, so that the deposits were approximately 12, 24, 36 and 48 sq. cs. in area, the rod being used to take the smallest area. In order that the cathodes should be dealt with simultaneously they were treated as follows. After being weighed they were dropped into holes in a stand, the holes being arranged to correspond with the final position of the cathodes in the cells. A carrier was dropped over them and clamped them tightly by means of thumb screws. The electrodes were now transferred to the cells. They were lowered gently into the electrolyte, so that no portion was wetted which did not finally remain immersed, the displaced liquid meanwhile being siphoned into the anode compartment. The carrier was removed and the current started. To wash the deposits the brass plates were swung out of the way, the carrier fixed in position, and the whole quickly transferred to a tank of water placed under the bench. After being thoroughly swilled the tubes were lowered into absolute alcohol contained in four large mouthed bottles, and allowed to stand whilst the carrier was removed. The electrodes were now withdrawn, wiped with a cloth, and placed in desiccators.

In order to detect any sources of error not previously considered the experimental conditions for each determination were varied as much as possible. These are set out in the accompanying Table (I.) for the 10 determinations. It will be seen that the current density varies from 0.14 to 0.0033, and the time of the experiments from 33 to 430 minutes. It may be mentioned that in the earlier series of determinations the strength of the copper sulphate solution varied from 0.5 to 2.5 normal with acid added from 0 to 20 per cent. with concordant results. The solution factor—*i.e.*, the mean loss of copper per unit area of the cathode is shown in column 8. This was obtained by substituting in the equation

$$w = ma + w_0,$$

where w = the weight of the copper deposit,

a = the area of the cathode,

w_0 = the intercept on the axis of zero area—*i.e.*, the value for the corrected weight of copper,

m = the slope of the line, or the solution factor.

This graph was compared to that drawn by eye; the latter was

sometimes difficult to draw where the experimental errors were large, due to the conditions imposed upon the experiment. In the majority of cases the two graphs agreed. In number (8) no satisfactory graph can be drawn, and therefore the solution factor was put equal to zero. The line for the three rods in number (3) as calculated has a small positive slope indicating oxidation. As the points were close together three colleagues were asked to draw the graph by eye. The mean value of the three intercepts was the same as that obtained from the equation. The factor for the tubes is also positive, but differs from that of the rods because they were not washed and dried at the same time. It is interesting to note that in these two cases the electrolyte has been boiled over copper for two hours, rendering it neutral. In determination (4), however, the electrolyte used in (3) has been treated in the same way three times. Its strength has dropped from 2 to 1.8 normal, whilst at the same time it has become acid, having a solution factor -6.1×10^{-5} . This clearly shows the necessity of correcting for solution under experimental conditions. The graphs as calculated and drawn by eye differ somewhat in determinations (6) and (7). The two values of the slopes are given, the calculated value being first. The mean value is used for the correction of the weights.

3. *The following is a typical example.*

Determination 10.

AgNO₃ solution = 1.9N, filtered.

CuSO₄ solution = 2.0N + 0.1 per cent. acid, but
used before in number 9.

Current = 0.3 ampere.

Time = 120 minutes.

Platinum Dishes.

	(1) grs.	(2) grs.
1st weight	32.26799	32.68371
2nd weight	34.70764	35.12310
1st weight of Ag	2.43965	2.43939
Loss on heating to redness	0.00051	0.00037
∴ Weight of AgNO ₃ occluded	0.00140	0.00104
∴ Weight of Ag deposited	2.43825	2.43835
Correction for weights	+1	+8
Correction for buoyancy	-6	-6
∴ Corrected weight of Ag	2.43820	2.43837
Mean weight of Ag	2.43829	

TABLE II.—WEIGHINGS.

No.	Corrected weight of silver.	Area of cathode. s.cs.	Weight of copper.	Correction for solution.	Corrected weight of copper.	Atomic weight of copper.	Mean error in atomic weight, due to	
							Cu.	Ag.
1 {	Grs.		Grs.	Grs.	Grs.	Grs.		
	2.21697	15.8	0.65274	+0.00032	0.65306	63.566	} 0.002	0.009
	2.21636	13.3	0.65282	0.00027	0.65309	63.569		
	...	10.0	0.65285	0.00020	0.65305	63.565		
2 {	...	14.8	1.27259	+0.00099	1.27358	63.565	} 0.002	0.000
	4.32294	12.3	1.27259	0.00082	1.27341	63.557		
	4.32294	9.6	1.27287	0.00064	1.27351	63.561		
	...	7.2	1.27298	0.00048	1.27346	63.559		
3 {	...	(a)41.3	0.64419	—0.00013	0.64406	63.559	} 0.004	0.010
	2.18669	29.0	0.64415	0.00009	0.64406	63.559		
	2.18601	(b)16.4	0.64428	0.00012	0.64416	63.569		
	...	14.8	0.64418	0.00011	0.64407	63.560		
	...	13.4	0.64425	0.00010	0.64415	63.568		
4 {	...	15.9	0.63167	+0.00097	0.63264	63.562	} 0.003	0.002
	2.14755	14.3	0.63175	0.00087	0.63262	63.559		
	2.14747	12.5	0.63179	0.00076	0.63255	63.553		
	...	10.7	0.63201	0.00065	0.63266	63.563		
5 {	3.24431	54.5	0.95210	+0.00360	0.95570	63.558	} 0.004	...
	*(3.24523)	44.1	0.95289	0.00292	0.95580	63.565		
	(3.24429)	24.7	0.95418	0.00163	0.95581	63.565		
	...	11.0	0.95491	0.00073	0.95564	63.554		
6 {	...	55.0	0.67569	+0.00104	0.67673	63.543	} 0.016	0.000
	2.29785	40.0	0.67648	0.00076	0.67724	63.591		
	2.29783	24.8	0.67654	0.00047	0.67701	63.569		
	...	11.2	0.67697	0.00021	0.67718	63.585		
7 {	...	53.2	1.04138	+0.00234	1.04372	63.570	} 0.011	0.022
	3.54120	41.8	1.04155	0.00184	1.04339	63.550		
	3.54370	23.0	1.04266	0.00101	1.04367	63.567		
	...	10.7	1.04280	0.00047	1.04327	63.543		
8 {	...	54.7	1.15430	} 0.00000 {	1.15430	63.563	} 0.018	0.005
	3.91789	46.0	1.15434		1.15434	63.565		
	3.91852	25.4	1.15362		1.15362	63.525		
	...	11.1	1.15486		1.15486	63.594		
9 {	...	53.1	1.42132	+0.00191	1.42323	63.555	} 0.002	0.026
	4.83364	41.8	1.42180	0.00151	1.42331	63.558		
	4.82973	23.9	1.42245	0.00086	1.42331	63.558		
	...	10.8	1.42281	0.00039	1.42320	63.554		
10 {	...	54.8	0.71782	+0.00036	0.71818	63.550	} 0.008	0.002
	2.43820	43.6	0.71815	0.00029	0.71844	63.573		
	2.43837	24.8	0.71812	0.00016	0.71828	63.559		
	...	12.0	0.71827	0.00008	0.71835	63.567		

* Note to No. 5.—A porous pot, after being allowed to run dry, invariably yields too high a weight for the silver. In this case a new pot was used, which had not been sufficiently boiled after its chemical treatment. If half of the occluded salt be taken as AgCN, then the corrected weight of the Ag deposit 3.24429 is in close agreement with the weight 3.24431. The bracketed weights have not been used in estimating the atomic weight.

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Copper.

Tubes	1.	2.	3.	Rod.
	Grs.	Grs.	Grs.	Grs.
1st weight	41.15292	37.81647	37.26446	32.95332
2nd weight	41.87035	38.53437	37.98221	33.67161
Weight of copper.....	0.71743	0.71790	0.71775	0.71829
Correction for buoyancy...	+30	+28	+27	+7
Correction for weights.....	+9	-3	+10	-9
Corrected weight of Cu (1)	0.71782	0.71815	0.71812	0.71827
Area of cathodes in s.cs. ...	54.8	43.6	24.8	12.0

These weights are plotted as ordinates against the corresponding areas as abscissæ. The line has a slope, which gives for the solution 0.66×10^{-5} grammes per square centimetre, and cuts the axis of zero area at the

corrected weight, 0.71831 gramme.

$$\therefore \text{The atomic weight of Cu} = \frac{0.71831}{2.43829} \times 107.88 \times 2.$$

$$= 63.562.$$

4. Experimental Errors.

In order to determine the extent of the experimental error, each copper weight is corrected for solution by adding to it the product of the area and the constant 0.66×10^{-5} . These corrected values are then compared with the mean silver as follows:—

Area of cathode.	Weight of Cu.	Correction for solution.	Corrected weight of Cu.	Atomic weight of Cu.
S.cs.	Grs.	Grs.	Grs.	
54.8	0.71782	+0.00036	0.71818	63.550
43.6	0.71815	0.00029	0.71844	63.573
24.8	0.71812	0.00016	0.71828	63.559
12.0	0.71827	0.00008	0.71835	63.567

Therefore the mean error in the atomic weight due to Cu = ± 0.008 . Similarly, if the corrected weight of copper 0.71831 is compared with the two silver weights 2.43820, 2.43837, the atomic weights become 63.564 and 63.560. Therefore the mean error in the atomic weight due to Ag = ± 0.002 . Table (II.) shows the weights, &c., for the 10 determinations, the atomic weight being calculated from the mean silver.

In determinations 7 and 9 the values for the atomic weight are vitiated by the large experimental errors of the silver. For this reason they are bracketed in the summary below and are omitted in determining the final value. These errors cannot

be accounted for, the deposits in both cases appearing remarkably good. Smith and Lowry (reference 18) pointed out that a strong solution of AgNO_3 has the power of dissolving AgNO_2 formed during the fusion of the salt. The nitrite may become insoluble in the weaker cathode solution and be deposited with the silver. Corrections made for occluded nitrite instead of the nitrate will raise the value for the atomic weight, but does not decrease the experimental errors. The source of error may be due to the detritus from the porous pots. If such is the case the error would increase with the duration of the experiment, and this seems to be the case.

The errors in the atomic weight due to copper depend largely on the state of the electrolyte.

For neutral solutions the error = 0.01, and greater still when CuO is added.

If 0.1 per cent. acid is added the error = 0.003 when the solution is used once.

If 0.3 per cent. is added the error = 0.002 when the solution is used several times.

Probably the errors are due to the presence of CuO formed by hydrolysis. This can be temporarily removed by filtering through fine Swedish filter paper, and permanently by adding enough acid or by electrolysing the solution. Any of these will impart to the solution the well-known clear sapphire colour.

5. Results.

Summarising the mean values for the 10 determinations we have :—

- (1) 63.567
- (2) 63.560
- (3) 63.563
- (4) 63.559
- (5) 63.560
- (6) 63.572
- (7) [63.558]
- (8) 63.562
- (9) [63.556]
- (10) 63.562

∴ The atomic weight of copper = **63.563**

when $\text{Ag} = 107.88$

Mean error in the atomic weight = ± 0.003

Mean error due to copper = ± 0.007

Mean error due to silver (omitting 7 and 9) = ± 0.003

Probable error due to weighing = ± 0.003

In these 10 determinations no less than 100 results can be obtained for the atomic weight whose mean value is 63.562.

In conclusion, the author takes this opportunity of putting on record his indebtedness to Dr. J. H. Vincent, in whose laboratory this work was done.

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ABSTRACT.

Four copper cells separating two silver cells were run in series. The areas of the four copper cathodes increased from 10 to 50 s.cs. By plotting the weights of the copper deposits against the corresponding areas of the cathodes, and extrapolating to zero area, the weight of the deposit is corrected for under experimental conditions.

The atomic weight of copper = $\frac{\text{corrected weight of Cu}}{\text{mean weight of Ag}} \times 107.88 \times 2$.

The mean atomic weight for 10 determinations = 63.563, with a mean error of ± 003 . To obtain a uniform coherent deposit of pure metal the following points were considered:—

1. Cylindrical cells with stationary and rotating cathodes were used.

2. The cathode current density must be kept below a certain *limiting* value to prevent the formation of non-coherent deposits, due to secondary deposition. This was found to depend upon the geometry of the cell, the concentration of the electrolyte, the presence of acid and other impurities, the addition of a porous pot and

the rate of revolution of the cathode. Formulæ are given by which the *limiting cathode current density* can be found for all conditions of the cell for Cu, Ag, Au and Zn.

3. To prevent the formation of loose crystalline clusters the current density must also be kept below a certain value depending upon the weight to be deposited. (Formulæ are given.)

DISCUSSION.

Mr. F. E. SMITH congratulated the author on the results of his work. He appeared to have triumphed over many difficulties, and for his particular purpose had converted the copper voltameter from an instrument of error into an instrument of precision. In future work he hoped that Mr. Shrimpton would avoid the use of common porous pots. They might produce trouble, and were not necessary, as all voltameter work could now be carried out without the introduction of any medium between anode and cathode. He should be pleased to give Mr. Shrimpton full particulars. The statement respecting deposition of hydrogen was, he thought, incorrect. It was not logical to assume that hydrogen ions were first deposited because of the lack of copper in the neighbourhood of the cathode, and then to state that as soon as they were deposited they went into solution again, and in doing so displaced copper from the solution. With regard to crystalline growths at the bottom of the cathode, he believed these were due to the high current density at the base due to the passage of the current through the liquid descending from the anode. There was also a possibility that the electrolyte was not quite pure. In the silver voltameter he had obtained striated deposits with impure electrolytes, but not with pure solutions. Mr. Shrimpton also stated that silver deposits from acidified solutions were normal; this was not his experience, nor that of other investigators. He believed the deposit to be less in mass when the electrolyte was acid. A rather important question arose with regard to any Cu_2SO_4 which might be formed in the cathode space. Richards (who also extrapolated to zero area, as Mr. Shrimpton had done) remarked in his Paper: "A value obtained in this way must correspond to a deposit of copper slightly too great; for the mode of correction (*i.e.*, extrapolation to zero area) does not take account of the growing, although slight, presence of cuprous salts." Mr. Shrimpton said the extrapolation to zero area covered this case. The speaker thought the point was one that should be settled. Of course, when one reduced the area the current density at the cathode was increased, and so also was the fall of potential near the cathode; this might have some influence.

Dr. J. H. VINCENT mentioned that after working out the conditions necessary for satisfactory results, the author had performed the 10 determinations quoted in the Paper straight away, no results being rejected. As they all came within 1 part in 6,000 of the mean there appeared to be no doubt that the correct conditions for satisfactory working had been obtained.

Dr. S. W. J. SMITH thought the author's views on secondary deposition could not be correct as they stood, although it was conceivable that sudden variations in the surface concentration of the copper sulphate, due to irregularities of convection, might make it possible for hydrogen to be deposited at one moment and to go into solution again at the next. Non-coherent deposits could be explained without invoking the aid of hydrogen. He thought the author's empirical conclusion, that the limiting current density depends upon the concentration of non-ionised molecules, had some theoretical support.

Mr. SHRIMPTON (communicated remarks): In section II. 2, line 34, as originally written, the author, following Hittorf, described the non-coherent deposit as being due to secondary reaction. As the deposit when the limiting current density was exceeded had the appearance of precipitated copper, it was assumed as a working hypothesis that the hydrogen after being deposited went again into solution, thereby displacing Cu from the unionised CuSO_4 . In the discussion it was pointed out that if the similar deposit of the Ag voltameter be carefully collected and weighed, there is a loss in weight, thus indicating the deposition of H. It seems, therefore, that the above hypothesis is unnecessary, the mere presence of deposited H materially affecting the deposition of the metal. For this reason the text has been altered. As regards the presence of acid in the silver cell, the author meant that the crystalline character of the deposit was not destroyed as in Cu, Zn and Au (the last in aqua regia). In the Ag cylindrical cell acid must not be present because non-coherent needles soon develop at the top of the deposit. Lastly, the author considers that Cu_2SO_4 , if formed, was completely corrected for, since its formation must be a function of the area of the cathode and the duration of the experiment. In the determinations the current density varied from 0.14 to 0.003, and the duration of the experiments from 33 to 430 minutes, yet no difference appears in the values for the atomic weight.